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H-bonded clusters in liquid ter-butanol through neutron diffraction

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Abstract : In the liquid state at room temperature, the neutron diffraction data of deuterated t-butanol exhibits a prominent pre-peak similar to what is known for long in the X-ray diffraction data with normal t-butanol This pre-peak is interpreted as a signature of hydrogen-bonded chain hexamer ring clusters in the liquid state.

Keywords H-bonded clusters, neutron diffraction, t-butanol

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1. Introduction

Alcohols are strongly hydrogen-bonded liquids where neighbouring molecules form chain clusters. It is now known that the chain hydrogen-bonded clusters in these liquids could give rise to what is called a pre-peak in the static diffraction data at small scattering vector (Q ~ 0.7 –0.8 Å $^{-1}$) before the main diffraction peak [1 – 3]. In X-ray diffraction data, these pre-peaks are known for long, while in neutron diffraction data, these are detected only recently [2, 4]. In the present case, we report the existence of such a pre-peak in neutron data of liquid t-butanol at room temperature. The cluster model of H-bonded closed hexamer chains, seems to produce well the pre-peak in the X-ray data of *t*-butanol [5] and so represents well the average liquid structure at room temperature. In the present communication, a preliminary analysis of first neutron data on deuterated liquid t-butanol is reported.

2. Experimental

A careful measurement was carried out on high-Q diffractometer at Dhruva, Bhabha Atomic Research Centre (BARC), Trombay, India following the conventional procedure. The liquid was a 99.8% deuterated sample supplied by Aldrich Ltd. (USA) and was held in vanadium can of 6 mm diameter and 0.1 mm thickness. The data collection and experimental corrections were done in usual manner and the cross-section data were normalized using a standard vanadium rod. The incident wavelengths of 0.783 Å and 1.278 Å were used and the data were recorded for an angular range 3° to 125°. The data show a very strong pre-peak at about Q = 0.71 Å $^{-1}$ (Figure 1) The inset exhibits Narten's X-ray data [3]. The complete set of corrected data is now available and detailed analysis of molecular structure, which would be reported separately, yields neutron total structure fuction H(Q) shown in Figure 2(a).

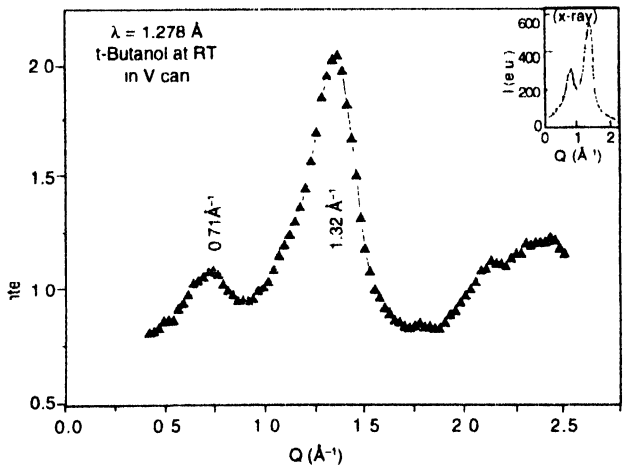

Figure 1. Intensity *vs.* Q plot

3. Interpretation of pre-peak

The interpretation of the pre-peak in terms of Fourier Transform (F. T.) of the diffraction data is difficult in view of the fact that it

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gives some modification in the correlations at distances 5–8 Å and definite features arising from the pre-peak are difficult to separate and clearly identify [1]. However, an interpretation in terms of the molecular chain cluster formation model is readily possible. The theory of molecular chain cluster formation due to hydrogen bonding has been discussed in several recent papers [6] and it is not repeated here. In the theory one assumes that (i) there exist distinct molecular cluster or clusters in the liquid due to hydrogen bonding and that (ii) the molecules in different clusters are orientationally uncorrelated. Assuming that for a large molecule like t-butanol the centre structure factor of the liquid can be approximately represented by the Percus-Yevick (PY) single site hard sphere model with suitable core diameter we can construct the model structure function of the liquid for any model cluster.

The X-ray data was checked for two widely suggested models – a closed chain hexamer and a linear chain tetramer. The hexamer chain model was shown to be more probable both in terms of total structure function and intermolecular radial distribution function (RDF) [5]. A more critical analysis of hexamer ring cluster model as a plausible model for t-butanol liquid structure in terms of asymmetrical part of the intermolecular correlation is presented in a recent communication [7]. For the interpretation of pre-peak in neutron data we have constructed hexamer closed chain cluster model similar to one

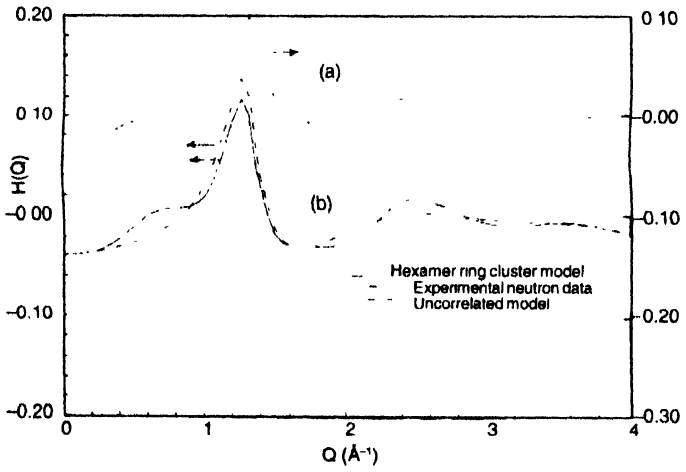

Figure 2. Total structure function *vs.* Q plot

for X-ray data. In the preliminary calculation for the model cluster, we have assumed methyl group CD_3 as a single unit with scattering length as sum of the scattering lengths of its constituents with the scattering centre located suitably. For the hard sphere centre structure, the hard core diameter is chosen to be 5.10 Å some what greater than that for the X-ray case [5] When the hexamer cluster parameters are suitably adjusted a model structure function of the form shown in Figure 2(b) is generated. The pre-peak is evident and the general features agree. For comparison, we also show the case where the neighbouring molecules are uncorrelated and as expected the pre-peak and the other features have disappeared.

In view of very good agreements with X-ray data [5, 7], we expect much better agreement for neutron data too. Further agreement however awaits, (a) Detailed consideration of the structure of the hexamer cluster model for neutron scattering because methyl group CD_3 cannot be treated as a single unit as in X-ray (CH_3), (b) The presence of fractions of other possible model clusters and (c) Combined analysis based on X-ray and neutron data. Works on these lines are in progress. It is, however true that the neutron diffraction data too supports the idea that the liquid t-butanol structure at room temperature is dominated by the presence of hexamer ring, closed chain units.

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